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Electrical measurements on ZTS single crystals

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Abstract : ZTS single crystals were grown by the free evaporation method from aqueous solutions. Electrical measurements were carried out along *a*-, *b*- and *c*-directions of the grown crystals at various temperatures by the conventional parallel plate capacitor method. The present study shows that the electrical parameters, *viz.* DC conductivity, dielectric constant, dielectric loss factor and AC conductivity increase with the increase in temperature. Activation energies were also determined.

Keywords : ZTS crystals, DC conductivity, AC conductivity, dielectric constant, dielectric loss, activation energy.

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$Zn(NH_2CSNH_2)_3SO_4$ crystal (zinc tris(thiourea) sulphate, ZTS), is a relatively new and promising semiorganic nonlinear optical material. Several investigators have shown considerable interest on this material and several reports [1–16] are already available. However, no report of electrical measurements at various temperatures on this material is available. In the present work, we have made an attempt to investigate the electrical (both DC and AC) properties of ZTS at various temperatures ranging from 40 to 150°C.

Analytical reagent (AR) grade samples of $ZnSO_4.7H_2O$ and thiourea along with double distilled water were used for the growth of single crystals. ZTS was synthesized at room temperature and supersaturated (0.15 M) aqueous solution was prepared by adopting the methods followed by previous workers [7]. Single crystals were grown at room temperature from the solution by the free evaporation method in the unstirred condition. Small crystals appeared in the beginning due to slow evaporation and grew larger (around 1 cm) in finite time (within two weeks). Best crystals were selected and used for the measurements.

The material of the grown crystal was confirmed by density, X-ray powder diffraction and FTIR spectral measurements. Density was measured by the floatation method. FTIR spectrum was recorded in KBr phase in the region 400 to 4000 cm^{-1} using the spectrophotometer available in the Regional Research Laboratory (CSIR), Thiruvananthapuram, India. X-ray powder diffraction data (in the 2θ range of 10 to 70° with $\lambda = 1.54056$ Å) were collected with the help of an automatic diffractometer available in the above place.

ZTS is thermodynamically stable atleast upto 200°C [17,18]. The electrical measurements were carried out at various temperatures ranging from 40 to 150°C along all the three (*a*-, *b*- and *c*-) directions. Crystals with high transparency and large defect-free size (> 3 mm) were selected and used for the electrical measurements. The extended portions of the crystals were removed completely and the opposite faces were polished and coated with good quality graphite to obtain a good ohmic contact.

The DC conductivity (σ_{dc}) measurements were carried out using the conventional two-probe (parallel plate capacitor) technique. The activation energy (E_{dc}) values were calculated using the σ_{dc} values [19,20].

The capacitance (C_{crys}) and dielectric loss factor (tan δ) were measured using the conventional parallel plate capacitor method with a fixed frequency (f) of 1 kHz

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using an LCR meter (Systronics make). Air capacitance (C_{air}) was also measured. As the crystal area was smaller than the plate area of the cell, parallel capacitance of the portion of the cell not filled with the crystal was taken into account and, consequently, the dielectric constant (ε_r) of the crystal was calculated by using the relation :

$$\varepsilon_r = \left(\frac{C_{crys} - C_{air}\left(1 - \frac{A_{crys}}{A_{air}}\right)}{C_{air}} \right) \left(\frac{A_{air}}{A_{crys}} \right),$$

where A_{crys} is the area of the crystal touching the electrode and A_{air} is the area of the electrode.

The AC conductivity (σ_{ac}) was calculated using the relation :

$$\sigma_{ac} = \varepsilon_0 \, \varepsilon_r \, \omega \tan \delta,$$

where ε_0 is the permittivity of free space (8.85 × 10^{-12} farad/m) and ω (= $2\pi f$) is the angular frequency. The activation energy (E_{ac}) values were estimated using the σ_{ac} values as done in the case of E_{dc} estimation.

The ZTS crystals grown in the present study are found to be stable, colourless and transparent. The morphology is similar to that reported in the literature [9, 17]. The FTIR spectrum and X-ray powder diffraction pattern obtained in the present study show that the grown crystals can be characterized as ZTS crystals.

The density value observed (within an accuracy of ±2%) in the present study (1.897 g/cc) is in good agreement with the literature values (1.923 g/cc [17] and 1.910 g/cc [18]) confirming the identity of the substance.

Tables 1 to 2 contain the σ_{dc} and activation energy values. Values of other electrical parameters obtained in the present study are shown in Figures 1 to 3. The ε_r values obtained in the present study for ZTS are of the same order with those obtained by Ramabadran *et al* [3] (measured at room temperature but with various frequencies).

Table 1. DC electrical conductivities.

Temperature (°C)	σ_{dc} (× 10^{-9} mho/m) along *a*- direction	*b*- direction	*c*- direction
40	0.605	1.545	1.252
50	0.675	2.148	1.261
60	0.689	3.352	1.275
70	0.781	6.446	1.305
80	0.816	24.645	1.385
90	1.243	64.456	1.726
100	1.520	164.300	2.244
110	2.026	310.345	2.736
120	3.039	523.707	3.506
130	4.757	863.847	5.342
140	6.591	1163.793	9.349
150	12.156	1675.862	13.516

Table 2. Activation energies.

Field direction (along)	E_{dc} (eV)	E_{ac} (eV)
a	0.337	0.086
b	0.856	0.100
c	0.276	0.085

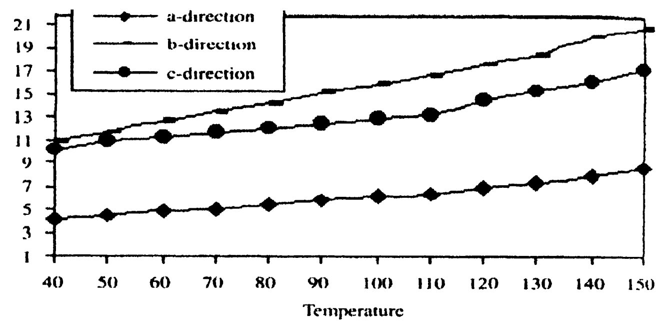

Figure 1. Variation of ε_r with temperature (°C).

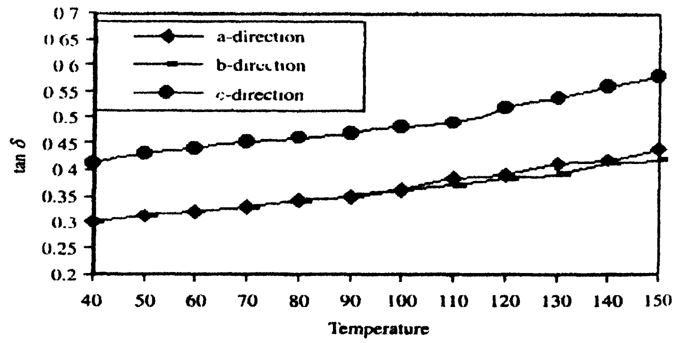

Figure 2. Variation of tan δ with temperature (°C).

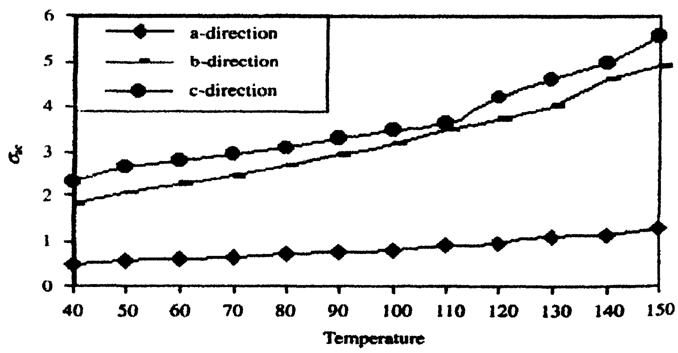

Figure 3. Variation of σ_{ac} (× 10^{-7} mho/m) with temperature (°C).

It can be seen that the σ_{dc}, ε_r, tan δ and σ_{ac} values increase with the increase in temperature along all the three (*a*-, *b*- and *c*-) directions. Also, following observations can be made from the results obtained in the present study :

σ_{dc} (along *b*-direction) > σ_{dc} (along *c*-direction) > σ_{dc} (along *a*-direction);

ε_r (along *b*-direction) > ε_r (along *c*-direction) > ε_r (along *a*-direction);

tanδ (along *c*-direction) > tanδ (along *a*-direction) > tanδ (along *b*-direction);

σ_{ac} (along *c*-direction) > σ_{ac} (along *b*-direction) > σ_{ac} (along *a*-direction);

E_{dc} (along *b*-direction) > E_{dc} (along *a*-direction) > E_{dc} (along *c*-direction); and

E_{ac} (along *b*-direction) > E_{ac} (along *a*-direction) > E_{ac} (along *c*-direction).

The increase of DC conductivity with the increase in temperature observed for ZTS in the present study is similar to that observed for systems like KDP [19,20]. The defect concentration will increase exponentially with temperature and consequently, the electrical conduction also increases. The conduction region considered in the present study seems to be connected to mobility of vacancies. The low activation energies observed suggests that oxygen vacancies may be responsible for conduction in this region.

The electrical conduction in the case of ZTS crystals may be considered in a similar way with that of KDP crystals as both are hydrogen bonded crystals. Also, the SO_4 group in ZTS and PO_4 group in KDP are tetrahedral in shape. The electrical conduction in KDP crystals has been established to be protonic. The possible type of point defects which help the electrical conduction process are the ionization defects produced as a result of proton jump from one phosphate group to another along the same bond and excess of positive charge. Migration of these defects may only modify electric polarization and may not change the charge at an electrode. The motion of defects occurs by some kind of rotation in the bond with defects. The speed of displacement $v = \upsilon a$, where a and υ are the distance and frequency respectively of the jump from one bond to the other [19].

Torres *et al* [21] have explained the conduction mechanism in tartrate crystals by the rotation of the tartrate ions. When the temperature of the crystal is increased there is a possibility of weakening of the hydrogen bonding system due to this rotation of the tartrate ion. This results in an enhanced conduction in these materials. In the case of ZTS also, the conduction mechanism may be explained by the rotation of the sulphate ions.

The dielectric constant of a material is generally composed of four types of contributions, *viz.* ionic, electronic, orientational and space charge polarizations. All these may be active at low frequencies. The nature of variations of dielectric constant with frequency and temperature indicates the type of contributions that are present in them. The dipolar orientational effect can be seen in some materials at high frequencies and ionic and electronic polarizations below 10^3 Hz. The large value of ε_r at low frequency and at low temperature is due to the presence of space polarizations which depends on the purity and perfection of the sample. Results obtained in the present study show that ionic polarization is dominating in the present system (ZTS crystals). Ramabadran *et al* [3] have reported that the dielectric constants of ZTS showed a very small variation with frequency over the range 100 Hz to 10 MHz and are about 25 % that of KDP only. The σ_{ac} and E_{dc} values are found to be more than the σ_{dc} and E_{ac} values respectively as expected for the dielectric samples.

The present study indicates that the σ_{dc}, ε_r, tan δ and σ_{ac} values increase with the increase in temperature. Proton movement and rotation of SO_4 ions may be attributed to the conduction process in ZTS crystals.

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